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REINFORCED CERAMIC MATERIALS WITH PHOSPHATE BINDERS

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The possibility of reinforcing ceramic materials based on zirconium dioxide and phosphate binders is investigated. The effect of the molding pressure, solid/liquid ratio, method of manufacture, content and type of reinforcing material, and various modifications of the initial material on the bending strength is shown.

One possible technology for making ceramic materials consists in using binders [1]. Examples of frequently used binders are aluminophosphate binder and orthophosphoric acid [2]. The present paper considers the possibility of producing ceramic materials using aluminophosphate binder (APB) and H_3PO_4.

With all their advantages, ceramic materials have a significant drawback, namely, brittleness, which restricts their use in industry. Other disadvantages include a complicated production technology, in particular, a high sintering temperature (1500 – 1700°C). Fiber reinforcement makes it is possible to obtain ceramics capable of deformation. In this case problems arise in connection with the interaction between the reinforcing fibers and the matrix material. As a consequence of chemical reactions at high sintering temperatures, the fibers disintegrate, and the material is not formed.

Zirconium dioxide was chosen to study reinforced ceramic materials. A technique that makes it possible to reinforce the material with fibers and sinter it at a lower temperature was used. Materials containing binders are of interest to researchers. Thus, compaction of the materials occurs at low temperatures, after which, when using certain binders, they cure at room temperature. Heat treatment of the materials obtained leads to a series of chemical transformations and, ultimately, to increased strength.

Materials on phosphate binders can be well compacted with different fillers, including metals [3].

The present paper considers the physicomechanical properties of materials based on zirconium dioxide. They can be a basis for heat-shielding materials and coatings, and in the future reinforced materials can be used in construction.

The phosphate binders used in preparing composite materials were orthophosphoric acid and APB. Phosphate binders are phosphate solutions resulting from dissolution of reactant phosphates in water or neutralization of acid (using oxides and hydroxides) [3]. A special feature of phosphate binders determining their wide application is their ability to form compounds at relatively low temperatures.

The reinforcing materials were carbon and aramide fibers and titanium wire with a treated surface. The surfaces of the reinforcing materials were treated with various agents to improve adhesion.

The effect of the technological factors (heat-treatment conditions, concentration of added liquid, solid/liquid mass ratio S/L) on the physicomechanical properties of the material was investigated.

In the first stage, samples made by casting into metal molds were studied. The initial components were technical zirconium dioxide and 86% orthophosphoric acid of density 1.72 g/cm^3. Mixtures were prepared by adding H_3PO_4 of various concentrations to zirconium dioxide. The mixtures were stirred to a homogeneous state and placed in molds. The mixture hardened only when heated to 270°C or more. The physicomechanical properties of materials based on zirconium dioxide and made by casting are given in Table 1.

TABLE 1

Sample*	S/L	Bending strength, MPa	Molds
1	2.14	2.60	Graphite-lubricated
2	1.32	2.00	The same
3	1.26	1.98	"
4	2.14	2.20	Non-lubricated
5	3.86	1.00	Copper
6	2.88	1.20	The same
7	2.32	0.90	"
8	1.92	1.90	"
9	1.92	0.50	Ceramic
10	1.45	0.50	The same
11	1.16	0.70	"

* Technical ZrO_2, binder: 86% solution of H_3PO_4.

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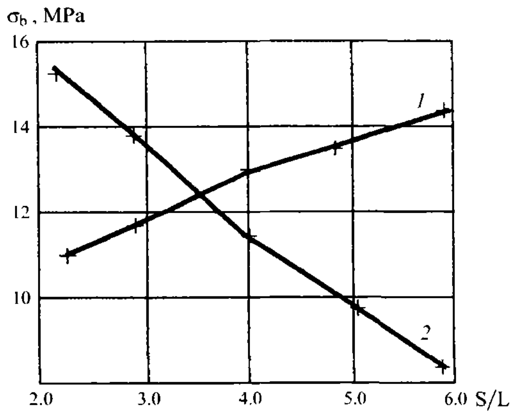

Fig. 1. Bending strength of samples σ_b versus S/L ratio: *1*) APB; *2*) H_3PO_4.

As can be seen, the bending strength of cast samples ranges from 0.5 to 2.6 MPa. The surface is rough, and large pores and cavities are seen on the fracture surface. Compression was used to increased the strength of the samples.

A molding mixture was prepared by adding orthophosphoric acid to the dry component (ZrO_2) or using APB as a binder. The dry component and the binder were mixed in certain ratios (S/L), and then samples were compressed and fired at a temperature up to 330°C (Fig. 1).

At S/L = 5.78 the bending strength of samples with APB-4 is almost twice that of samples with H_3PO_4, and as the ratio S/L decreases, the strength of the samples with H_3PO_4 increases, and the strength of the samples with APB, on the other hand, significantly decreases. Figure 2 shows the relationship between the sample strength and the molding pressure.

Fiber-reinforced materials were analyzed. The reinforcing materials were carbon and aramide fibers and titanium wire. The effect of the quantity of the reinforcing component on the bending strength of the sample was investigated (Fig. 3).

With increasing quantity of introduced material, the strength decreases linearly. This is presumably due to the ab-

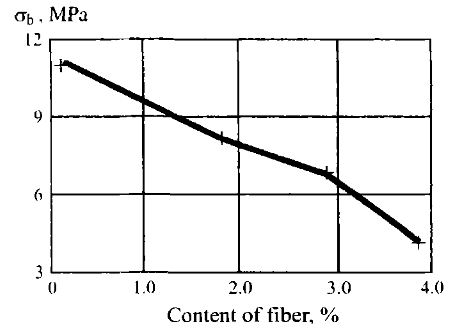

Fig. 3. Bending strength σ_b of reinforced material versus the content of carbon fiber.

sence of adhesion between the fiber and the matrix, and in this case the fiber acts as a pore-forming material. To eliminate this disadvantage, coupling agents of various compositions were deposited on the fiber surface [4].

The results of strength tests of composite materials based on zirconium dioxide reinforced with aramide and carbon fibers are represented in Table 2. The highest bending strength was achieved in samples reinforced with carbon fiber dressed with sodium hexafluorosilicate Na_2SiF_6. However, the strength of these samples is inferior to the strength of samples of the same composition without reinforcement.

The effect of acid of various concentrations on the strength of the sample was studied in composites with carbon fibers (Table 3).

The effect of various modifications of the initial material on the bending strength of samples was studied as well. The experiments involved technical ZrO_2 (1), ultradisperse ZrO_2 with a particle size less than 0.1 μm (2), zirconium dioxide in the form of microfibers obtained in laboratory experiments (3), and a mixture of these materials in equal mass fractions (4). The results are given in Table 4.

It can be seen that when using H_3PO_4 the highest strength level is achieved in microfiber ZrO_2. The microfibers are crystals with a length/diameter ratio ranging from 1 : 10 to 1 : 20 [5]. The best result for composite materials

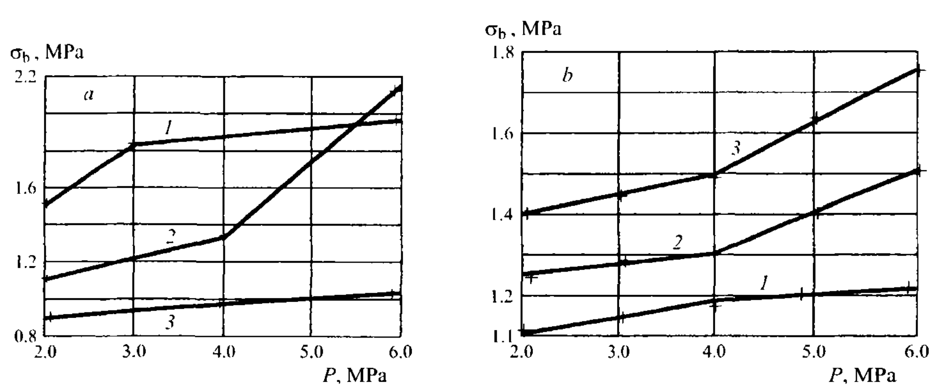

Fig. 2. Bending strength σ_b versus molding pressure *P* for samples based on H_3PO_4 (*a*) and APB (*b*). S/L ratio: *1*) 2.88; *2*) 3.86; *3*) 5.78.

TABLE 2

Sample*	Bending strength, MPa	Reinforcing material
1	16.30	Carbon fiber treated with Na_2SiF_6
2	2.36	Carbon fiber treated with APB
3	3.00	Aramide fiber treated with HF and APB
4	2.50	The same
5	3.70	Pulverized carbon fiber treated with HF
6	3.60	The same

* Technical ZrO_2, binder: 86% solution of H_3PO_4. Molding pressure 40 MPa.

based on APB was recorded for technical ZrO_2. Thus, the cast materials have high porosity and can be used as heat-insulating materials.

When the added liquid was orthophosphoric acid, the resulting materials had higher strength than in the case of APB.

The use of carbon and aramide fibers as a reinforcing material does not increase the strength of the ceramic material, since the interaction between the fiber and the matrix is weak.

After treating the carbon fiber with various coupling agents, it was found that Na_2SiF_6 increases the interaction between the fiber and the matrix, which increases the strength of the material.

Reinforcement of the ceramics with microfiber ZrO_2 leads to increased bending strength compared to ceramics reinforced with carbon and aramide fibers.

TABLE 3

Sample*	Content of H_3PO_4, %	S/L	Bending strength, MPa
1	58.5	7.60	5.5
2	76.0	6.34	10.2
3	86.0	5.80	16.3

* Technical ZrO_2, reinforcing material: carbon fiber. Molding pressure 40 MPa.

TABLE 4

Zirconium dioxide*	Binder	Bending strength of samples, MPa
1	86% H_3PO_4	15.40
2	The same	14.00
3	"	17.60
4	"	15.60
1	APB-4	19.20
2	The same	16.80
3	"	12.80
4	"	7.87

* Molding pressure 20 MPa; S/L = 5.78.

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